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Light scattering as an alternate probe of fractal structure of the AgI colloidal aggregates

Traian Nicula

Military Chemistry Application School, Str. Marasti 48, Campulung-Arges, 0425, Romania

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Abstract In this paper, we discuss developments that lead to significant advances in the understanding of colloidal aggregation. The key of this advances is the recognition that the random, disordered clusters that are produced when colloids aggregate have dilation symmetry, and objects that possess it are called fractals.

Light scattering techniques are based on the fact that, in the limit of weak scattering, intensity $S(q)$ of the scattered beam is simply a Fourier transform of $c(r)$, the autocorrelation function. Thus, one has a method to make an *in situ* measurement of the correlation function, and hence the fractal dimensions. Our experimental results referred to AgI colloids.

Keywords Light scattering, fractals, AgI colloidal aggregates

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1. Introduction

Kinetic aggregation has historically been one of the most widely studied subjects within colloid science, as it represents a problem in classical statistical physics of great fundamental interest as well as a widely exploited phenomenon of great technological importance. The structure of colloid aggregates can be quantitatively characterized, despite their very random and disorder appearance, thus resolving one of the major problems that limited the study of kinetic colloid aggregation.

2. Colloid aggregation

Most of the emphasis of the theoretical work has been on the structure of the clusters [1,2]. The aggregates appear universally to possess dilation symmetry. There are two natural length scales that can be associated with each aggregate, the radius of the individual particles, a, and the size of the whole cluster, R. However, between these two length scales, $a<<r<<R$, the dilation symmetry means that there are no other characteristic lengths and that, in a statistic sense, the structure of the aggregates is invariant under a change of length scale.

The mass of the clusters scales with their characteristic size as $M \approx R^{d_f}$, where the fractal dimension d_f, is typically not an integer and is less than the Euclidean dimension of space, d, in which the aggregate is embedded. In addition, the mass-mass correlation function within the cluster also exhibits power law behavior, $c(r) \approx r^{-\alpha}$ where $\alpha = d - d_f$. Thus, the fractal dimension of the clusters offers a quantitative characterization of their structure, and allows us to distinguish rather subtle differences, which can result from different types of aggregation.

3. Light scattering

The scattering techniques are based on the fact that, in the limit of the weak scattering, the intensity, $S(q)$, of the scattered beam is simply a Fourier transform of $c(r)$, from real space into momentum space, where q is the scattered wavevector. This relationship is true for all types of scattering, including, for example, light, X-ray and neutrons. The measured $S(q)$ will exhibit not only the scale invariant correlation of the fractal regime, but also the effects of the fact that these fractal correlation expend only over a finite regime. An analytic expression for $S(q)$ from fractal aggregates has been developed by Sinha *et al.* [3]. In q-space, the scattering structure factor for an aggregate has the form :

$$S(q, R) = C(q)F^2(qa), \tag{1}$$

where the $F(qa)$ is the form factor for the scattering from a single sphere of radius a. The square of the form factor, $F^2(qa)$, has the property that at $qa << 1$, $F^2(qa) = 1$, while at large qa, $F^2(qa)$ gives the familiar Porod scattering, which for sphere exhibits $\approx q^{-4}$ behavior. Furthermore, we note that in the fractal regime of the scattering $a << q^{-1} << R$, the scattering behaves as $S(q, R) \approx (qR)^{-d_f}$, or using the scaling of the mass and the cluster size, $S_M(q) \approx M^{-1} q^{-d_f}$ Thus, in principle, the fractal dimension can be determined directly from the scattering.

The actual scattering intensity from the cluster is then

$$I_M(q) = M^2 S_M(q), \tag{2}$$

where M is the mass of the cluster of size R. There are two problems that must be considered to ensure that the light scattering can be properly interpreted by our discussion above. First, we must check that the scattering is weak enough so not to be distorted by multiple scattering Secondly, we must consider whether the polydispersity in the cluster mass distribution distorts our measurements[4].

The total scattering intensity from the distribution of the clusters is

$$I(q) = \int N(M) M^2 S_M(q)\, dM, \tag{3}$$

where $N(M)$ is the cluster mass distribution. For $qR >> 1, S_M(q) \approx 1/Mq^{d_f}$, thus the intensity is

$$I(q) \approx \int N(M) M dM, \tag{4}$$

that is simply the first moment of the distribution function. The scattering accurately reflect the fractal structure of the aggregates, if the size of the clusters measured by the first moment is sufficiently large that $qR >> 1$ for all q used. This was ascertained by monitoring the scattered intensity as the colloid aggregated, and waited until the intensity was independent of time at all q.

4. The fractal nature of the AgI colloids

Since AgI is sparingly soluble in water, the colloids were prepared by mixing the dilute solutions of $AgNO_3$ and KI of concentration n/100 in different proportion. The colloids obtained were diluted to avoid multiple scattering from different clusters. The scattering within a single cluster is weak enough to avoid multiple scattering [5]. Using a spectrophotometer the colloid samples were made to have the same concentration by monitoring the extinction $E = \lg I_0/I$ to be the same.

As it was mentioned, the scattering will accurately reflect the fractal structure of the aggregates if the scattered intensity $I(q)$ is independent of time at all q, so we waited for every colloid sample to fulfil this condition. To reveal the fractal structure of the colloid samples, we measured the scattered intensity $I(q)$ as a function of the scattering wavevector q, than we plotted the intensity as a function of q in a logarithmic plot. For all the colloid samples, we obtained a straight line. Thus, the scattering exhibits the power law behavior expected for a fractal and the slope gives the fractal dimension d_f. The ratios of the concentration of the reagents for the sample prepared and the fractal dimensions d_f, are given in Table 1.

Table 1 The ratios of the concentration of the reagents for the sample prepared and the fractal dimensions d_f

C $AgNO_3$ C KI	d_f
29·1	2.88 ± 0.05
5 1	2.72 ± 0.05
2 1	2.53 ± 0.05
1 1	2.28 ± 0.05
1.2	1.75 ± 0.05
1 5	1.61 ± 0.05

From Table 1, we remark the connection ratios of the reagent concentrations and the fractal dimensions. The fractal dimensions of the samples do not seem to be in agreement with the cluster-cluster aggregation model [6-8]. The CCA model is usually defined on a square lattice with periodic boundary conditions in which N initial particles are distributed randomly. These particles diffuse by performing a Brownian motion on the lattice and, if they occupy adjacent sites at a given time, they will stick together irreversibly and give rise to larger clusters. These clusters move with a probability of motion proportional to the diffusion coefficient.

The value of the fractal dimension of the clusters obtained from computer simulation is

$$d_f \cong 1.80\ (\pm 0.05) \text{ for } d = 3\ [8]. \tag{5}$$

In particle-cluster aggregation, the particle trajectory plays a crucial role. In fact, it is the trajectory that determines the density of the structure (*i.e.*, the fractal dimension). For this reason, it is interesting to consider the relationship between the dimensionality of the particle walk and the fractal dimension of the aggregates. It is possible to use a generalization of the random walk in which the length of the step x follows a random distribution, satisfying the condition

$$p(x \geq \lambda) = \lambda^{-l}\ , \tag{6}$$

where the probability $p(x \geq \lambda)$ is the probability that the length of the step will be greater than or equal to λ. This type of trajectory with $1 < f < 2$ is called Levy flight and has a dimensionality equal to f. The fractal dimension depends on the values of the parameter f, which describes the Levy flight trajectory.

This model is able to explain the continuous variation of the fractal dimension, but it is a particle cluster aggregation model that does not take into account the cluster-cluster aggregation. From the values shown in Table 1, we remark that there are fractal dimensions smaller than the fractal dimension of the cluster-cluster aggregation model ($d_f = 1.80$).

The best fit to the experimental data of Table 1 is a power law equation of the following form (Figure 1)

$$y = 0.7x^{-0.53}, \tag{7}$$

where $y = d - d_f$ ($d = 3$, Euclidean dimension) and x is reagents concentration ratios. It is striking the fact that it is obtained as a power law behavior because fractal spatial autocorrelation functions and the probability density for Levy flight are also power laws with the exponent a rational number.

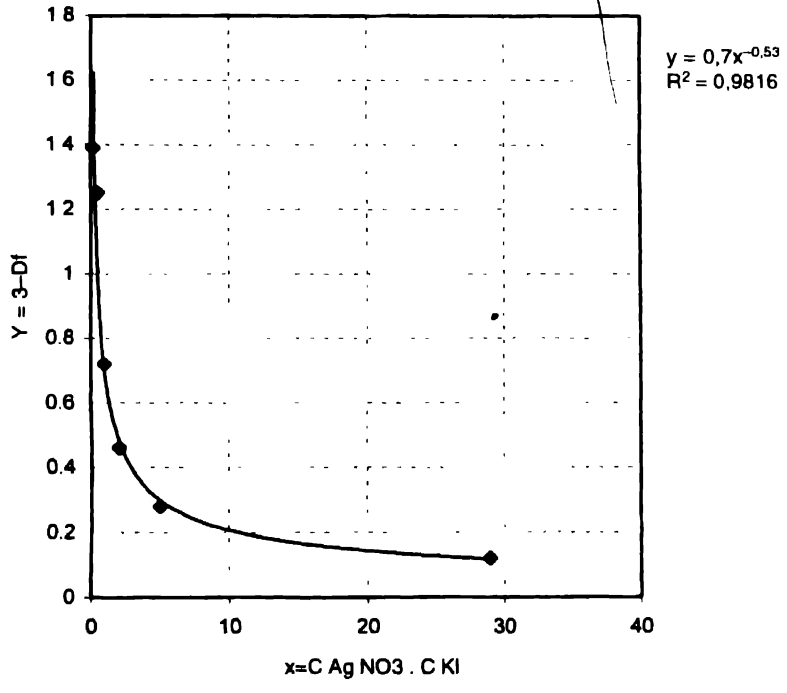

Figure 1. The plot shows the variation of the quantity $3-d_f$ with reagents concentration ratio.

5. Conclusions

The ability to quantitatively characterize the structure of the aggregates by measuring their fractal dimensions has allowed us to distinguish the relatively subtle changes that occur when they are formed. It should be possible to use the scattering techniques to study aggregates formed under a wide variety of different conditions, and compare the structures of the clusters

obtained in a quantitative manner. Thus, the application of these techniques and analyses should lead to a better understanding of a variety of colloidal aggregation processes.

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References

[1] *Kinetic Aggregation and Gelation*, eds F Family and D P Landau (Amsterdam Elsevier) (1984)

[2] D W Schaefer, J E Martin and D S Cannell *Phys Rev Lett* **52** 2371 (1984)

[3] S K Sinha, T Freltoftand and J Kjems in *Kinetic Aggregation and Gelation*, eds F Family and D P Landau (Amsterdam Elsevier) p 87 (1984)

[4] J E Mann and B J Ackerson *Phys Rev* **A 31** 1180 (1985)

[5] D A Weitz and J S Huang *Phys Rev Lett* **54** 1416 (1985)

[6] P Meakin *Phys Rev Lett.* **51** 1119 (1983)

[7] R Jullien and R Botet in *Aggregation and Fractal Aggregates* (Singapore World Scientific) (1987)

[8] T Vicsek in *Fractal Growth Phenomenon* (Singapore World Scientific) (1992)